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⑰ Foaming surfactant compositions.

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EP 0070074 B1

Description

Technical field

This invention relates to surfactant combinations which provide controllable aqueous foams. Such compositions can be used in any situation where foams are desirable, including the laundry, personal cleaning products, dishwashing, fire fighting, oil well drilling, ore beneficiation, solution mining, washing hair, preparation of foamed solid structures, etc.

Description of the prior art

Alkylpolyglycosides which are surfactants have been disclosed in U.S. Patents 3,598,865; 3,721,633; and 3,772,269. These patents also disclose processes for making alkylpolyglycoside surfactants and built liquid detergent compositions containing these surfactants. In US 3,721,633, anionic synthetic detergents can be present, in amounts of from 0 to 1 part by weight of anionic detergent per part of alkyl glycoside. U.S. Patent 3,219,658 discloses alkylmonoglucosides and suggests their utility as foam stabilizers for other surfactants. Various polyglycosides surfactant structures and processes for making them are disclosed in U.S. Patents 2,974,134; 3,640,998; 3,839,318; 3,314,936; 3,346,558; 4,011,389; 4,223,129.

Foaming compositions containing an alkylpolysaccharide surfactant, and anionic cosurfactants and possibly an auxiliary foam booster, have been disclosed in copending published EP—A—0 070 075 and EP—A—0 070 076.

Light duty detergent compositions containing an alkylpolysaccharide, alkylbenzene sulfonate and alkylpolyethoxylate sulfate cosurfactants are known from copending published EP—A—0 070 077.

All percentages, parts and ratios used herein are by weight unless otherwise specified.

Summary of the invention

This invention relates to the discovery of certain combinations of surfactants which provide unusual foams. Specifically this invention relates to foaming compositions comprising

(1) an alkylpolysaccharide surfactant having the formula $RO(R^1O)_Z$, wherein Z is a moiety derived from a reducing saccharide containing from 5 to 6 carbon atoms, preferably a glucose, galactose, glucosyl, or galactosyl residue or mixtures thereof, R is a hydrophobic group selected from the group consisting of alkyl, alkyl phenyl groups and mixtures thereof in which said alkyl groups contain from about 8 to 18 carbon atoms preferably from about 10 to about 16 carbon atoms, most preferably from about 12 to about 14 carbon atoms said alkyl groups being either saturated or unsaturated and containing from 0 to 3 hydroxy groups; R^1 is ethylene, propylene and/or glyceryl, t is from 0 to about 30, preferably 0 to about 10, most preferably 0; wherein x is a number from about 1.5 to about 10, preferably 1.5 to 4, most preferably 1.6 to 2.7; and

(2) an anionic cosurfactant which is a sulfate, sulfonate and/or carboxylate or mixtures thereof neutralized with one or more cationic moieties (M) to complete the formula, preferably the anionic cosurfactant has the formula



wherein R^2 is an alkyl, alkylphenyl, hydroxyalkylphenyl or hydroxyalkyl, or mixtures thereof, said alkyl groups containing from about 6 to about 30 carbon atoms, preferably about 10 to about 18 carbon atoms; y is a number from 0 to about 4, z is a number from 0 to about 4, y+z is at least 1, and M is a cationic moiety with q being selected to complete the formula, wherein the ratio (2) to (1) is from 1:10 to 10:1, except that

(1) The weight ratio of (2) to (1) is superior to 1:1 when the anionic surfactant is an alkalimetal alkylbenzenesulfonate and when in the general formula for the alkylpolysaccharide $t=0$ and Z is a glycoside radical;

(2) The weight ratio of (2) to (1) is at least 1:2 when the anionic cosurfactant is soap; and

(3) When the anionic cosurfactant does not contain a sulfonate or carboxylate it must be from 1.5 to 3 and the alkylpolysaccharide surfactant must have a free fatty alcohol content of less than 2% by weight.

It has surprisingly been found that the cosurfactants interact with the alkylpolysaccharide surfactant of this invention to provide a relatively stable foam which is readily rinsed.

The invention also relates to the process of producing foams utilizing aqueous solutions containing from about 0.01% to about 95% of the mixed surfactants.

Description of the preferred embodiments

The alkylpolysaccharide surfactant

The alkylpolysaccharides are those having a hydrophobic group containing from about 8 to about 18 carbon atoms, preferably from about 10 to about 16 carbon atoms, most preferably from 12 to 14 carbon atoms, and a polysaccharide hydrophilic group containing from about 1.5 to about 10, preferably from 1.5 to 4, most preferably from 1.6 to 2.7 saccharide units (e.g., galactoside, glucoside, fructoside, glucosyl, fructosyl and/or galactosyl units). Mixtures of saccharide moieties may be used in the alkyl polysaccharide surfactants. The number x indicates the number of saccharide units in a particular alkylpolysaccharide surfactant. For a particular alkylpolysaccharide molecule x can only assume integral values. In any physical

sample of alkylpolysaccharide surfactants there will in general be molecules having different x values. The physical sample can be characterized by the average value of x and this average value can assume non-integral values. In this specification the values of x are to be understood to be average values. The hydrophobic group (R) can be attached at the 2-, 3-, or 4-positions rather than at the 1-position, (thus giving e.g. a glucosyl or galactosyl as opposed to a glucoside or galactoside). However, attachment through the 1-position, i.e., glucosides, galactosides, fructosides, etc., is preferred. In the preferred product the additional saccharide units are predominately attached to the previous saccharide unit's 2-position. Attachment through the 3-, 4-, and 6-positions can also occur.

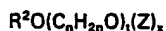
Optionally and less desirably there can be a polyalkyoxide chain joining the hydrophobic moiety (R) and the polysaccharide-chain. The preferred alkoxide moiety is ethoxide.

Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from about 8 to about 20, preferably from about 10 to about 16 carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to 3 hydroxy groups and/or the polyalkyoxide chain can contain up to about 30, preferably less than 10, most preferably 0, alkoxide moieties.

Suitable alkyl polysaccharides are decyl, dodecyl, tetradecyl, hexadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexaglucoisides, galactosides, lactosides, fructosides, fructosyls, lactosyls, glucosyls and/or galactosyls and mixtures thereof.

The alkylmonosaccharides are relatively less soluble in water than the higher alkylpolysaccharides. When used in admixture with alkylpolysaccharides, the alkylmonosaccharides are solubilized to some extent. The use of alkylmonosaccharides in admixture with alkylpolysaccharides in a preferred mode of carrying out the invention. Suitable mixtures include coconut alkyl, di, tri-, tetra-, and pentaglucoisides and tallow alkyl tetra-, penta-, and hexaglucoisides.

The preferred alkyl polysaccharides are alkyl polyglucosides having the formula



wherein Z is derived from glucose, R^2 is a hydrophobic group selected from the group consisting of alkyl, alkylphenyl and mixtures thereof in which said alkyl groups contain from about 10 to about 18, preferably from 12 to 14 carbon atoms; n is 2 or 3, preferably 2, t is from 0 to about 10, preferably 0; and x is from 1.5 to about 8, preferably from 1.5 to 4, most preferably from 1.6 to 2.7. To prepare these compounds a long chain alcohol (R^2OH) can be reacted with glucose, in the presence of an acid catalyst to form the desired glucoside. Alternatively the alkylpolyglucosides can be prepared by a two step procedure in which a short chain alcohol (C_{1-6}) is reacted with glucose or a polyglucoside ($x=2$ to 4) to yield a short chain alkyl glucoside ($x=1$ to 4) which can in turn be reacted with a longer chain alcohol (R^2OH) to displace the short chain alcohol and obtain the desired alkylpolyglucoside. If this two step procedure is used, the short chain alkylglucoside content of the final alkylpolyglucoside material should be less than 50%, preferably less than 10%, more preferably less than 5%, most preferably 0% of the alkylpolyglucoside.

The amount of unreacted alcohol (the free fatty alcohol content) in the desired alkylpolysaccharide surfactant is preferably less than about 2%, more preferably less than about 0.5% by weight of the total of the alkyl polysaccharide plus unreacted alcohol. The amount of alkylmonosaccharide is about 20% to about 70%, preferably 30% to 60%, most preferably 30% to 50% by weight of the total of the alkylpolysaccharide. For some uses it is desirable to have the alkylmonosaccharide content less than about 10%.

As used herein, "alkylpolysaccharide surfactant" is intended to represent both the preferred glucose and galactose derived surfactants and the less preferred alkylpolysaccharide surfactants. Throughout this specification, "alkylglycoside" is used to include alkylglycosides because the stereochemistry of the saccharide moiety is changed during the preparation reaction.

The anionic cosurfactants

Anionic cosurfactants can be selected from the group consisting of sulfates, sulfonates, carboxylates and mixtures thereof. The cosurfactants are neutralized with a cationic moiety or moieties selected from the group consisting of alkali metal, e.g. sodium or potassium, alkaline earth metal, e.g. calcium or magnesium, ammonium, substituted ammonium, including mono-, di-, or tri-, ethanolammonium cations. Mixtures of cations can be desirable. The anionic cosurfactants useful in the present invention all have detergent properties and are all water-soluble or dispersible in water.

Alkylbenzene sulfonates

One of the preferred cosurfactants for use in this invention is an alkylbenzene sulfonate. The alkyl group can be either saturated or unsaturated, branched or straight chain and is optionally substituted with a hydroxy group. Middle phenyl positions are generally preferred for volume of foaming in light soil conditions. However, in heavier soil conditions, phenyl attachment at the 1- or 2-position is preferred.

The preferred alkylbenzene sulfonates contain a straight alkyl chain containing from about 9 to about 25 carbon atoms, preferably from about 10 to about 13 carbon atoms, and the cation is sodium, potassium, ammonium, mono-, di-, or triethanolammonium, calcium or magnesium and mixtures thereof. Magnesium is the preferred cationic moiety. These same cations are preferred for other anionic surfactants and

ingredients. The magnesium alkylbenzene sulfonates where the phenyl group is attached near the middle of the alkyl chain are surprisingly better than the ones with the phenyl near the end of the chain when the polysaccharide chain averages greater than about 3 saccharide units. Suitable alkylbenzene sulfonates include C₁₁ alkylbenzene sulfonates with low 2-phenyl content (i.e. majority of phenyl groups attached uses the middle of alkyl chain).

The alkylbenzene sulfonate cosurfactant is desirable in the foaming compositions of the invention since the foams produced therewith are exceptionally stable, have a large volume, rinse quickly, and do not have a "slippery" feel. These compositions are particularly desirable for industrial and commercial processes as discussed hereinafter. The volume of foam produced using the alkylbenzene sulfonate cosurfactant is larger than for any other cosurfactant.

Soap

Other preferred cosurfactants for use in this invention are carboxylates, e.g. fatty acid soaps and similar surfactants. The soaps can be saturated or unsaturated and can contain various substituents such as hydroxy groups and alpha-sulfonate groups. Preferably, the hydrophobic portion of the soap is a straight chain saturated or unsaturated hydrocarbon. The hydrophobic portion of the soap usually contains from about 6 to about 30 carbon atoms, preferably from about 10 to about 18 carbon atoms. The use of carboxylate cosurfactants is especially valuable since the alkylpolysaccharide surfactants are exceptional lime soap dispersers.

The cationic moiety (M) for carboxylate cosurfactants is selected from the group consisting of alkali metal, for example, sodium or potassium, alkaline earth metal, for example, calcium or magnesium, ammonium, or substituted ammonium, including mono-, di-, or triethanolammonium cations. Mixtures of cations can be desirable.

In addition to the preferred alkylbenzene sulfonate and soap cosurfactants many other surfactants which contain sulfonate or carboxylate groups can be used in the foaming compositions of the invention. Generally the use of these latter cosurfactants produces less foam volume than does the use of the preferred cosurfactants. However, the alkylpolysaccharide surfactant stabilizes the foams which are produced and allows the foams to be rinsed more quickly.

One group of cosurfactants that are of interest because of their superior detergency are the zwitterionic detergents which contain both a cationic group, either ammonium, phosphonium, sulfonium or mixtures thereof and a sulfonate or carboxylate group. Preferably there are at least about four atoms separating the cationic and anionic groups. Suitable zwitterionic surfactants are disclosed in U.S. Patents 4,159,277; 3,928,251; 3,925,262; 3,929,678; 3,227,749; 3,539,521; 3,383,321; 3,390,094; and 3,239,560, incorporated herein by reference. Such cosurfactants are especially desirable for shampoos.

Another group of cosurfactants are the amphoteric detergents which have the same general structure as the zwitterionic surfactants but with an amine group instead of the quaternary ammonium group.

Yet other cosurfactants are the alkyl (paraffin or olefin) sulfonates, preferably with a more central hydrophilic group, containing from about 6 to about 30 carbon atoms. Compositions containing these cosurfactants produce the least volume of foam, if that is desired. The hydrophobic group can contain up to about 10 hydroxy groups and/or ether linkages. Examples include C₁₄₋₁₈ paraffin sulfonates and C₁₄₋₁₈ olefin sulfonates.

Still another cosurfactant is a soap structure containing up to about 10 ether linkages in the chain and from about 1 to about 4 carbon atoms between ether linkages with from about 6 to about 30 carbon atoms in a terminal portion containing no ether linkages.

The preferred alkylpolyglucosides that contain an average of from 1.5 to 4 glucoside units, preferably from 1.6 to 2.7 glucoside units; less than about 50% short chain alkylpolyglucosides; less than about 10%, preferably less than about 2%, most preferably less than about 0.5% unreacted fatty alcohol, increase the sudsing ability of conventional sulfate detergent cosurfactants, especially alkyl sulfate and alkyl polyether sulfate cosurfactants having the formula:



wherein R³ is an alkyl or hydroxyalkyl group containing from about 8 to about 18 carbon atoms, n is 2 or 3, t can vary from 0 to about 30, and M is a cationic moiety as defined above, the cosurfactant being water soluble or dispersible.

A preferred foaming composition of the invention herein comprises:

(1) an alkylpolysaccharide surfactant having the formula RO(R'¹O)_t(Z)_x wherein Z is a moiety derived from a reducing saccharide containing from 5 to 6 carbon atoms and wherein R is a hydrophobic group selected from the group consisting of alkyl, alkylphenyl and mixtures thereof in and which said alkyl groups contain from about 8 to about 18 carbon atoms, R¹ is ethylene, propylene and/or glyceryl, t is from 0 to about 30; and x is a number from about 1.5 to about 10, preferably 1.5 to 4, most preferably 1.6 to 2.7; and

(2) a mixture of cosurfactants neutralized with one or more cationic moieties consisting essentially of:

(a) from about 1% to about 95% preferably about 10% to about 50% of a water soluble alkylbenzene sulfonate cosurfactant in which the alkyl group contains from about 10 to about 13 carbon atoms, and

(b) from about 5% to about 99%, preferably 50-90% of a cosurfactant selected from the group

consisting of an alkyl glyceryl ether sulfonate in which the alkyl group contains from about 8 to about 18 carbon atoms, an alpha-olefin sulfonate in which the olefin group contains from about 10 to about 18 carbon atoms, an alkyl polyethoxylate carboxylate in which the alkyl group contains from about 10 to about 18 carbon atoms, and the polyethoxylate chain contains from about 2 to about 6 ethoxylate groups, and mixtures thereof.

Such compositions have improved suds mileage as compared to compositions containing only the alkyl benzene sulfonate cosurfactant and the alkylpolysaccharide surfactant.

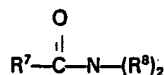
Another preferred embodiment of a foaming composition of the invention herein comprises:

(1) an alkylpolysaccharide surfactant having the formula $RO(R^1O)_t(Z)_x$, wherein Z is a moiety derived from a reducing saccharide containing from 5 to 6 carbon atoms and wherein R is a hydrophobic group selected from the group consisting of alkyl, alkylphenyl and mixtures thereof in which said alkyl groups contain from about 8 to about 18 carbon atoms; R¹ is ethylene, propylene and/or glyceryl; t is from 0 to about 30; and x is a number from about 1.5 to about 10;

(2) is anionic cosurfactant selected from the group consisting of sulfates, sulfonates, carboxylates and mixtures thereof neutralized with one or more cationic moieties M to complete the formula, the ratio of (2) to (1) being from about 1:10 to about 10:1, and

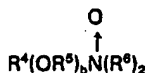
(3) from about 2% to about 10% of an auxiliary foam booster selected from the group consisting of:

(a) amides having the formula



wherein R⁷ is an alkyl group containing from about 8 to about 18 carbon atoms, preferably about 12 to about 14 carbon atoms and each R⁸ is the same or different and is selected from the group consisting of hydrogen, C₁₋₃ alkyl, C₁₋₃ alkanol, and $-(\text{C}_2\text{H}_4\text{O})_{1-4}\text{H}$ groups and mixtures thereof;

(b) amine oxides having the formula:



wherein R⁴ is an alkyl group containing from about 8 to about 18 carbon atoms, preferably from 12 to 14 carbon atoms, each R⁵ contains two or three carbon atoms, b is from 0 to about 30, each R⁶ is the same or different and is selected from the group consisting of C₁₋₃ alkyl, C₁₋₃ alkanol, and $-(\text{C}_2\text{H}_4\text{O})_{1-6}\text{H}$ groups and mixtures thereof; and

(c) mixtures thereof.

Such compositions provide superior grease/oil removal and suds mileage.

Preferred anionic cosurfactants are alkylbenzene sulfonate, alpha-olefin sulfonate, alkylsulfates, alkylpolyethoxylate sulfates and paraffin sulfonates and mixtures thereof. The cationic moieties are selected from the group consisting of sodium, potassium, ammonium, monoethanolammonium, diethanolammonium, triethanolammonium, calcium, magnesium and mixtures thereof.

Preferred compositions of this embodiment of the invention comprise from 1% to about 95%, preferably 5% to about 50% of an alkylpolysaccharide surfactant in which the alkyl group contains from 12 to 14 carbon atoms, x is from 1.5 to 4, more preferably 1.6 to 2.7; from 1% to about 95%, preferably from about 10% to about 50% of an anionic cosurfactant neutralized with one or more cationic moieties and which is a mixture of

(1) from 1% to about 95%, preferably from about 5% to about 50% of an alkyl benzene sulfonate in which the alkyl group contains from about 8 to about 13 carbon atoms or an alpha-olefin sulfonate in which the olefin group contains from about 10 to about 18 carbon atoms, or mixtures thereof; and

(2) from 1% to about 95%, preferably from about 5% to about 50% of an alkyl polyethoxylate sulfate in which the alkyl group contains from about 8 to about 18 carbon atoms, preferably from 12 to 14 carbon atoms and from about one to about six ethoxylate moieties and wherein from about 1% to about 100%, preferably from about 10% to about 80% of the cationic moieties are magnesium; and

wherein the auxiliary foam booster is an amide.

Another preferred foaming composition of the invention herein is an agglomerated light duty detergent granule composition comprising

(1) from about 5% to about 60%, preferably from 10% to about 20% of an alkylpolysaccharide surfactant having the formula $RO(R^1O)_t(Z)_x$, wherein Z is a moiety derived from a reducing saccharide moiety containing from 5 to 6 carbon atoms and wherein R is a hydrophobic group selected from the group consisting of alkyl, alkylphenyl and mixtures thereof in which said alkyl groups contain from about 8 to about 18 carbon atoms, preferably from 12 to 14 carbon atoms; R¹ is ethylene, propylene and/or glyceryl; t is from 0 to about 30; and x is a number from about 1.5 to about 10, preferably 1.5 to 4, most preferably 1.6 to 2.7;

(2) from about 5% to about 60% of an alkyl benzene sulfonate cosurfactant in which the alkyl group

contains from about 10 to about 13 carbon atoms, said alkyl benzene sulfonate neutralized with one or more cationic moieties (M) to balance the formula;

(3) from about 5% to about 60%, preferably from about 10% to about 20% of an alkylpolyethoxylate sulfate cosurfactant in which the alkyl group contains from about 10 to about 16 carbon atoms and in which there are from 1 to about 6 ethoxylate groups, said alkylpolyethoxylate sulfate neutralized with one or more cationic moieties M to complete the formula;

(4) from about 5% to about 80% of a water soluble inorganic salt selected from the group consisting of sodium and potassium sulfates, chlorides, carbonates, phosphates, and mixtures thereof.

10 The processes

Mixtures of alkylbenzene sulfonate and/or the soap cosurfactant and the alkylpolysaccharide surfactant can be used at levels of from about 0.01% to about 95%, in ratios of cosurfactant to alkylpolysaccharide of from about 10:1 to about 1:10, in water with agitation to provide foams. These foams are relatively stable and, if not disturbed, can exist for several days. Furthermore, the foam has structural integrity and does not spread out. The foams prepared using mixtures of alkylbenzene sulfonate and the alkylpolysaccharide are unique in that they do not have a "slippery" feel. All of the foams rinse quickly.

The unusual properties of the foams of this invention make them valuable for use not only in soap bars, bubble baths, shaving creams, laundry, dishwashing, and washing hair, where a good volume of stable suds and quick rinsability are desirable, but also in a large number of fields unrelated to detergency.

20 The compositions and processes of this invention are particularly valuable for use in the "foam" or "mist" well drilling processes in which the foam is used to carry water and/or soil particles to the surface of the bore hole. A description of such a drilling method can be found in U.S. Patents 3,303,896; 3,111,178; 3,130,798; and 3,215,200; incorporated herein by reference. In such a process, the surfactants are present at a level of from about 0.01% to about 5%, preferably from about 0.01% to about 2%, most preferably from about 0.05% to about 0.5%. The preferred cosurfactant is an alkylbenzene sulfonate.

25 The compositions and processes of this invention are also of considerable value in fire fighting or fire prevention processes where a stable foam is used to extinguish a flame or sparks by cutting off the oxygen supply. This includes fire fighting and foaming runways for crash-landings as disclosed in U.S. Patents 2,514,310; 3,186,943; 3,422,011; 3,457,172; 4,479,285; and 3,541,010, incorporated herein by reference. Concentrations of from about 0.1% to about 5% are useful.

30 The compositions and processes of this invention are also especially valuable in the field of preparing gypsum board, plastic, and resin foams. The foams of this invention provide a stable relatively thick structure permitting solidification of the resins, plastics, cellulosic particles, etc., into stable foam structures having light densities, thick cell walls and good structural integrity. Examples of forming processes which utilize foaming agents are described in U.S. Patents 3,669,898; 4,907,982; 4,423,720; and 4,423,720, incorporated herein by reference.

35 The flotation of minerals so as to concentrate the mineral values, e.g., in the foam (beneficiation), can be carried out advantageously using the compositions and processes of this invention. Such processes are described in U.S. Patents 4,147,644; 4,139,482; 4,139,481; 4,138,350; 4,090,972; and 3,640,862, incorporated herein by reference.

40 A special advantage of the compositions and processes of this invention involves making use of their exceptional stability to provide temporary insulation for plants when freezing conditions are expected. An alkylbenzene sulfonate is the preferred cosurfactant and the foam can be applied to the foliage etc. of the plants. Such a process is disclosed in U.S. Patent 3,669,898, incorporated herein by reference.

45 The range of utilities which are possible with the compositions and processes of this invention include all of the above and many more.

Typical compositions for use as light duty liquid detergent compositions in washing dishes comprise from about 5% to about 50%, preferably from about 10% to about 40% of the mixture of surfactants disclosed hereinbefore. From about 1% to about 50% of a solvent selected from the group consisting of C₁₋₃ alkanols, C₁₋₃ alkanolamines, C₂₋₄ polyols, mixtures thereof, and the balance water. It is a special advantage of the compositions of this invention that they can be made in concentrated form (up to about 50% by wt. of the mixture of surfactants) with only very low levels of organic solvents and without the addition of expensive hydrotropic materials. Additional suds boosters or builders such as trialkyl amine oxides and fatty acid amides can also be used in amounts up to about 20%. Fatty alcohols should not be used.

55 Shampoo compositions comprise from about 1% to about 95%, preferably from about 5% to about 20% of the mixture of surfactants mentioned hereinbefore, from about 1% to about 5% of an alkanol amide, from about 0.5% to about 3% of a polymeric thickener, and the balance water. It is a special advantage of the shampoos that they rinse quickly and readily.

60 Additional ingredients

The compositions and processes of this invention can utilize other compatible ingredients, including other surfactants, in addition to the mixture of surfactants herein disclosed. In detergent compositions the compositions can contain any of the well known ingredients including minor amounts of other surfactants, 65 detergency builders, soil suspending agents, brighteners, abrasives, dyes, fabric conditioning agents, hair

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conditioning agents, hydrotropes, solvents, fillers, clays, perfumes, etc. Suitable ingredients are disclosed in U.S. Patents 4,166,039—Wise; 4,157,978—Llenado; 4,056,481—Tate; 4,049,586—Collier; 4,035,257—Cherney; 4,019,998—Benson et al; 4,000,080—Bartolotta et al; and 3,983,078—Collins, incorporated herein by reference. The shampoo compositions of this invention can contain any of the additional ingredients known to the art to be suitable for use in shampoos. Listings of suitable additional ingredients, including low levels of other surfactants can be found in U.S. Patents 4,089,945; 3,987,161; and 3,962,418, incorporated herein by reference.

Of special interest are ingredients which modify the feel of aqueous solutions containing the foaming compositions of this invention. For example, raising the pH to above about 8.5 by alkaline materials or incorporating the tertiary alcohols of the European patent application No. 0 049 546, published on April 14, 1982. Such ingredients are desirable for some consumers since the solutions do not have the normal "soapy" feel associated with surfactant solutions.

The following nonlimiting examples illustrate the foaming compositions of the present invention.

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Example I Relative volume of suds comparison and consumer preference

	A	B	C
	Generic commercial product U.S. crystal White®	Premium commercial product U.S. Palmolive®	Product of the invention
Formula	Weight %	Weight %	Weight %
Sodium C ₁₁₋₁₃ alkyl benzene sulfonate	10.5	18.0	18.0
C ₁₂₋₁₃ alkylpolyglucoside ₂₋₃ (>2% free fatty alcohol)	—	—	12.0
Sodium C ₁₄₋₁₅ alkyl polyethoxylate ₃ sulfate	5.5	12.0	—
Balance of formula inc. water	84.0	70.0	70.0
Sudsing			
Relative Volume of Suds (ml) 0.2% solutions	110	125	220
Consumer test			
Overall preference. %	10	18	23
Favorable sudsing comments. %	74	85	80
Favorable rinsing comments. %	3	6	10

The foaming composition of the invention is superior to a representative generic product and at least equivalent to a representative premium commercial product and is preferred by consumers for rinsing reasons. The test involved 50 consumers washing soiled dishes in the test solutions. The consumers wore rubber gloves during the test. The differences are significant at the 95% confidence level for the invention over the generic product.

The relative volume of suds in ml. is determined by the following test procedure:

100 ml of the test solution at 46.1°C is placed in a 500 ml graduated cylinder: the solution is agitated by repeated inversion of the graduated cylinder until the amount of suds in the cylinder does not increase with further agitation. Suds height is measured directly on the cylinder scale making allowance for the height of liquid remaining in the cylinder. The test solution is made by adding the test product to water having a hardness of 0.12 grams per liter (Ca/Mg=3/1).

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Example II
LAS suds boosting

Wt. % of:	A	B	C	D	E	F	G
Sodium C _{11.8} alkyl-benzene sulfonate	0	20	40	50	60	80	100
C ₁₂₋₁₅ alkylpoly ₂₋₃ glucoside	100	80	60	50	40	20	0
Relative Volume of suds (ml)	140	220	280	300	310	300	240

The suds (foam) were generated as described in Ex. 1 using 300 ppm of the surfactant mixtures in city water (0.15 grams per liter). The results clearly show the sudsing synergism for ratios greater than about 1:2; The foaming composition of the invention herein correspond to formulae E, F, G=Compositions A to D are known from US-A-5721633.

Example III
Soap suds boosting

Wt. % of:	A	B	C	D	E	F
Sodium oleate	0	20	40	60	80	100
C ₁₂₋₁₅ alkylpoly ₂₋₃ glucoside	100	80	60	40	20	0
Relative Volume of suds (ml.)	160	270	280	300	310	260

The suds were generated as in Ex. 1 using 500 ppm, of the surfactant mixtures. This data clearly indicates the sudsing synergism for the foaming composition of the invention herein.

Example V
Foaming with soap
Effect of hardness on relative volume of suds

	Grains hardness			
	0	2	4	6
Sodium oleate	225	10	0	0
Sodium oleate plus C ₁₂₋₁₅ alkylpoly ₂₋₃ glucoside (3:2 ratio)	360	100	55	10

The suds were generated as in Ex. 1 using 500 ppm. of the surfactant mixtures.

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Example V

Alkyl polyglucoside (C_{12-15} alkylpoly $_{2-3}$ glucoside)

Suds boosting for the following representative cosurfactants (3:2 ratio; 500 ppm)

	% increase in foaming
Sodium $C_{11.8}$ alkylbenzene sulfonate	100—150
Sodium oleate	50—75
3-[N-coconutalkyl-N,N-dimethyl]- 2-hydroxy-1-sulfonate	40—60
Sodium C_{14-15} olefin sulfonate	20—40
Sodium coconut alkyl sulfate	10—30
Sodium coconut alkyl polyethoxyate ₃ sulfate	0—20

The above data clearly demonstrate the criticality of utilizing a carboxylate or sulfonate anionic detergent cosurfactant for sudsing synergism with the alkyl polyglucoside surfactant.

Example VI

Glucoside chain length criticality

40:60 wt. ratio of C_{12-15} alkyl polyglucoside to sodium C_{12} alkylbenzene sulfonate (500 ppm. concentration) where the glucoside portion is:

	Relative volume of suds (ml)
Monoglucoside	180
Diglucoside	240
Pentaglucoside	260
Decaglucoside	170
Sodium $C_{11.8}$ alkylbenzene sulfonate alone	160

"Diglucoside" etc. indicates the average glucoside chain length in the sample is two, etc. As can be seen from the above, significant synergism is obtained only with 1.5 or more glucoside units and preferably less than about 10, more preferably less than about 8 glucoside units.

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Example VII
Alkylbenzene sulfonates (LAS)
Homologs/phenyl-position (3:2 ratio; 500 ppm)

	Relative volume of suds (ml)
Ex. II's alkylpolyglucoside plus:	
Sodium C ₁₁ LAS, high* 2-phenyl	210
Sodium C ₁₁ LAS, low** 2-phenyl	250
Sodium C ₁₂ LAS, high 2-phenyl	225
Sodium C ₁₂ LAS, low 2-phenyl	225
Sodium C ₁₄ LAS, high 2-phenyl	210
Sodium C ₁₄ LAS, low 2-phenyl	215

As can be seen from the above, in general C₁₁, low 2-phenyl LAS is preferred for sudsing.

*phenyl group attached over the end of the alkyl chain
**phenyl group attached near the middle of the alkyl chain.

Example VIII
Suds boosting of alkyl polyglucosides and effect of soil

	Relative volume of suds (ml)		
	Without soil	With soil*	
		0.5%	1.0%
0.2% aqueous solution of a detergent composition formulated with: 15% sodium C _{11.8} alkyl- benzene sulfonate (C _{11.8} LAS)	120	50	25
15% C _{11.8} LAS+12% Ex. II's alkyl polyglucoside	310	130	70
30% C _{11.8} LAS	190	140	100

*Test method of Ex. I modified by adding to the test solution the indicated amount of soil. % is wt.% of test solution.

The soil is a 44%/56% by weight mixture of Fluff® and PREP® both of which products are available in the United States from The Procter & Gamble Company.

As can be seen from the above, the benefit for the invention is even more remarkable when soil is present.

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Example IX Relative volume of suds (ml)

		No soil	1% soil* present
5	Generic commercial product (Crystal White®)**	110	30
10	Premium commercial product B (Palmolive Liquid®)	120	100
	Premium commercial product C (Joy®)	125	120
15	12% C _{11.8} LAS/8% Ex. II's alkyl polyglucoside	180	120
	18% C _{11.8} LAS/12% Ex. II's alkyl polyglucoside	240	150
20	24% C _{11.8} LAS/16% Ex. II's alkyl polyglucoside	300	180

*Soil is added as described in Ex. VII.

25 **Crystal White® is available from Colgate-Palmolive Co.
Palmolive Liquid® is available from Colgate-Palmolive Co.
Joy® is available from The Procter & Gamble Company.

30 Suds generated as in Ex. I using a test solution containing 0.2% by wt. of the indicated commercial product or 0.2% of a product formulated with the surfactant mixtures shown.

As can be seen, the simple mixtures of surfactants representative of this invention can be formulated to be superior, or at least equal, to even the best light-duty dishwashing liquids.

Example X

35	Wt. % of;	A	B	C	D	E	F
	C _{11.8} LAS (Sodium)	0	20	40	60	80	100
40	Sucrose monolaurate	100	80	60	40	20	0
	Relative Volume of suds (ml.)	30	100	150	190	210	220

45 300 ppm of surfactant mixture used in test solution of Ex. I.
The above demonstrates that structures which are similar to the alkyl polyglucosides do not provide the benefits of this invention.

Example XII Shampoo

50	Alpha-olefin sulfonate (40% aqueous solution)	30.00%
	Ex. I's alkyl polyglucoside	3.00%
55	Hydroxyethyl cellulose	0.80%
	Perfume	1.00%
60	Preservative	0.04%
	Distilled water q.s.	100.00%

65

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Example XIII
Paraffin sulfonate suds boosting

Wt. % of:	A	B	C	D	E	F
Mixture of sodium C ₁₄₋₁₅ paraffin sulfonate	0	20	40	60	80	100
C ₁₂₋₁₅ G ₄₋₅ *	100	80	60	40	20	0
Relative Vol. of Suds (ml)	185	250	275	275	235	210

Test Conditions:

Total concentration of 300 ppm; water having 8 grains of mixed hardness.

*C₁₂₋₁₅ G₄₋₅ is a notation of an alkyl polysaccharide surfactant in which there are 4—5 glucoside units and in which the alkyl group has 12—15 carbons.

Example XIV
Sodium vs. magnesium alkylbenzene sulfonate
Relative volume of suds (ml.)

	Without soil		With soil*	
			0.6%	1.0%
0.2% aqueous solution of a detergent composition with: 15% Ex. II's alkyl polyglucoside; 22% C _{11.8} alkylbenzene sulfonate with the benzene group attached primarily to the center of the alkyl chain, sodium neutralized		450	150	75
15% Ex. II's alkyl polyglucoside; 22% C _{11.8} alkylbenzene sulfonate with the benzene group attached primarily to the center of the alkyl chain, magnesium neutralized		450	200	110
Premium product (Joy®)		350	120	75

*Soil added to the test solution as in Ex. VIII.

Example XV

The optimum alkylpolysaccharides, especially alkylpolyglucosides have an HLB* of from about 6 to about 27 and a critical micelle concentration (CMC)** of less than about 1000 ppm, preferably less than about 500. Short chain alkylpolysaccharides in which the alkyl group contains less than about 8 carbon atoms have unacceptably high CMC's and those alkylpolysaccharides having more than about 4 saccharide units have unacceptably high HLB's as is shown in the following table in which the alkyl group and the glucoside chain length were varied.

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	# of Glucosides # of Carbons		G ₀	G ₁	G ₂	G ₃	G ₄	G ₅
5	C ₄	HLB	5.1	12.4	17.9	23.3	28.8	34.2
	C ₆	HLB	4.2	11.4	17.0	22.4	27.8	33.2
10	C ₈	HLB	3.2	10.5	16.0	21.4	26.9	32.3
		CMC		~7000				
	C ₁₀	HLB	2.2	9.6	15.0	20.4	26.0	31.4
15		CMC		~700	2000E			
	C ₁₂	HLB	1.3	8.6	14.1	19.5	25.0	30.4
20		CMC	~6.0	~70	~200	225E		~250
	C ₁₄	HLB	0.4	7.6	13.2	18.6	24.0	29.4
		CMC		~6	~20	25—60E		
25	C ₁₆	HLB	0.0	6.7	12.2	17.6	23.1	28.5
		CMC	~0.3	~0.6	~4			
30	C ₁₈	HLB	0.0	5.8	11.2	16.6	22.2	27.6
		CMC			~1			

E=estimated

35 *HLB determined according to Davies: Proc. & International Congress, Surface Activity 1,426, Butterworths, London, 1957.

**ppm

40 As can be seen above, (1) longer pure glucoside chain lengths raise the HLB and lower the molecule's surface activity (high CMC) and (2) the shorter alkyl chain lengths have extremely high CMC's even as the monoglucoside.

Example XVI The following formulas were prepared:

		A	B	C
45	Magnesium linear C _{11,2} alkylbenzene sulfonate	22.4	22.4	22.4
50	C ₁₂₋₁₃ alkylpolyglucoside (G _{1,7}) (<2% free fatty alcohol)	14.9	14.9	14.9
55	C ₉₋₁₁ alkoxypropyldi-hydroxyethyl amine oxide	—	4	—
	C ₁₂ alkyl dihydroxy ethyl amine oxide	—	—	4
60	Ethanol	5	5	5
	Water	balance	balance	balance

65 Formulas A, B and C were compared by generating suds with a constant source of agitation under

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standard conditions (1 gal. water, 115°F. (46.1°C) 0.12 g. hardness in a 3 gal. (11.3 l) dishpan using a standardized mixture of fat plus protein, carbohydrate and edible acid). Dinner plates are washed with 4 ml. of soil on each plate and the suds height is measured after each five plates. 30 plates in total are washed and the integral of the suds height taken over the number of plates washed is reported as the SDW grade (SDW=Suds During Washing).

	A	B	C
SDW grade	24	28.8	28.4

This shows that the addition of a small amount of these amine oxides dramatically increases the amount of dishes that can be washed. Similar results are obtained when a fatty acid amide, e.g., a coconut fatty acid amide, diethanol amide, and/or isopropanol amide is substituted, at least in part for the specific amine oxides.

Example XVII

105 grams of sodium dodecylbenzene sulfonate are mixed with 350 grams of anhydrous sodium sulfate. After the mixture is ground into a fine powder, 70 g of C₁₂₋₁₃ alkylpolyglucoside (G_{2.2}) (<2% free fatty alcohol) are then mixed in. The mixture is transferred into a fluid bed dryer operated at room temperature (e.g., Aeromatic Inc., Model STREA-1), then 100 grams of a 50% solution of said alkylpolyglucoside is sprayed onto the powder. 7.5 milliliters of a 1% polar blue solution are sprayed onto the powder and a small portion of perfume is then added. The resulting granule is dried in a vacuum oven at 30 in. (762 mm) of Hg vacuum at 50°C for ten hours to remove excess water.

Example XVIII

Ammonium C_{11,2} linear alkyl benzene sulfonate was admixed with C₁₂ alkylpolyglucoside G_{3.5} in a ratio of about 2:1. The mixture was used at a level of 400 ppm in city water. The initial suds volume was more than 300 ml., but after the addition of about 1.25 grams of a standard grease soil per 200 ml. of wash solution, the suds had disappeared. Substitution of a sodium C₁₂₋₁₆ alkyl glyceryl ether sulfonate for 25% and 40% of the mixture extended the point at which there was no suds to 1.5 and 1.75 grams of soil per 200 ml. of wash solution respectively.

Similar results are obtained when a sodium, potassium, ammonium, or monoethanolammonium C₁₂₋₁₆ alkylpolyethoxy₃ acetate, or C₁₄₋₁₆ olefin sulfonate or mixtures thereof is substituted for at least part of the alkyl glyceryl ether sulfonate.

Example XIX

The following formula was prepared with alkylpolyglucosides having 0.3% and 1% free fatty alcohol respectively.

	Wt. %
Ammonium C _{11,2} linear alkyl benzene sulfonate	17.5
Magnesium C _{11,2} linear alkyl benzene sulfonate	6.4
Ammonium C ₁₂₋₁₃ alkyl polyethoxylate (0.8) sulfate	6.1
C ₁₂₋₁₃ alkylpolyglucoside G _{1.7}	5
Minors and water	balance

The SDW values for the low (0.3%) and high (1%) free alcohol samples were 12.9 and 12.2 respectively with an LSD_{0.05} at 0.6. See Ex. XVI for test method.

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Example XX

The following formulas were prepared:

	A	% by weight		D
		B	C	
5	Ammonium/magnesium C _{11,2} linear alkyl benzene sulfonate	24.2	21.8	—
10	Ammonium/magnesium C ₁₂₋₁₅ olefin sulfonate	—	—	12.8
15	Ammonium/magnesium C ₁₂₋₁₃ alkyl sulfonate	—	—	19.2
	Ammonium C ₁₂₋₁₃ alkyl polyethoxylate (0.8) sulfate	6.5	5.8	—
20	C ₁₂ fatty acid diethanol- amide	—	3.8	—
25	C ₁₂₋₁₃ alkylpolyglucoside G _{1.7} (free fatty alcohol <0.5%)	5.3	4.8	4
	Minors and water	balance		
30		A	B	C
	The SDW Index	79	89	97
				107

The SDW index is the SDW grade for each product as a percentage of the SDW value of a standard commercial product.

The following are examples of particularly preferred compositions. The broad and preferred ranges of ingredients which can be used are given in the second and third columns, respectively, in each example.

	Example XXI		
		% by weight	
40	Ammonium C _{11,4} alkyl benzene sulfonate	17.5	10—35
45	Magnesium C _{11,4} alkyl benzene sulfonate	6.4	0—11
	Ammonium C ₁₂₋₁₃ alkyl poly- ethoxylate (0.8) sulfates	6.1	2—11
50	C ₁₂₋₁₃ alkyl polyglucoside (1.7) derived from glucose (<0.5% free fatty alcohol)	5.0	2—11
55	Ethanol	3.7	0—10
	Ammonium xylene sulfonate	3.0	0—10
60	H ₂ O & minor components, e.g., perfume	Balance	

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Example XXII

% by weight

5	Ammonium C ₁₂₋₁₃ alkyl sulfate	15.7	7-23	10-20
	Sodium C ₁₄₋₁₆ olefin sulfonate	10.4	4-19	6-13
10	MgCl ₂ · 6H ₂ O	5.6	0-11	2-10
	Coconut monoethanol amide	5.5	2-8	3-7
15	C ₁₂₋₁₃ alkyl polyglycoside (1.7) derived from glucose (<0.5% free fatty alcohol)	5.9	2-12	3-9
	Ethanol	4.0	0-10	0-10
20	H ₂ O and minor components, e.g., perfume		Balance	

The alkyl groups in the surfactants of Examples XXI and XXII can vary from about 10 to about 16 carbon atoms and the cations can be ammonium, sodium, potassium, monoethanolammonium, diethanolammonium, triethanolammonium, magnesium, or preferably, mixtures thereof. Any of the preferred alkyl polyglycosides can be used and other known amine oxide and amide suds boosters disclosed herein can be used.

Example XXIII

When a 2:1 mixture of an ammonium C_{11,2} alkylbenzene sulfonate and the C₁₂₋₁₃ alkylpolyglucoside (2-4) (<2% free fatty alcohol) are tested under the conditions of Example II the initial suds volume is good, but the SDW grade is not as good as some premium commercial products. Substitution of between 25% and 50% of the mixture with a sodium C₁₂₋₁₆ alkyl glyceryl ether sulfonate, or sodium C₁₄₋₁₆ olefin sulfonate, or sodium C₁₂₋₁₃ alkyl polyethoxylate₍₃₎ acetate increases the SDW grade without lowering the initial sudsing excessively.

Known analytical techniques can be used to determine the structures of the alkylpolysaccharide surfactants herein; for example, to determine the glycosidic chain length, the amount of butyl glucoside, the free fatty alcohol content, and the level of unreacted polysaccharide. More specifically, gas or liquid chromatography can be used to determine the unreacted alcohol content and the unreacted polysaccharide content respectively. Proton nmr can be used to determine the average glycosidic chain length. The point of attachment of the hydrophilic portion of the molecule to the hydrophobic portion of the molecule can be determined by ¹³C nmr.

The alkylpolysaccharide surfactants are complex mixtures. Their components vary depending upon the nature of the starting materials and the reaction by which they are prepared. Analytical standards which are useful in calibrating instruments for analyzing the components of a particular alkylpolysaccharide surfactant can be obtained from Calbiochem Behring Co. LaJolla, California. These standards include those for octylglucoside (Calbiochem #494559), decylglucoside (Calbiochem #252715), dodecylmaltoside (Calbiochem #3243555).

The HLBs of alkylpolysaccharide surfactants useful in the foaming compositions of this invention have the values given in Example XV, the CMCs will approximate those values given in the same example. Alkylpolysaccharide surfactants having the structures specified in the claims and characterized by one or more of the standard analytical techniques will give the results indicated in the examples.

Claims

1. A foaming composition comprising:
(1) an alkylpolysaccharide surfactant having the formula



wherein Z is a moiety derived from a reducing saccharide containing from 5 to 6 carbon atoms; R is a hydrophobic group selected from the group consisting of alkyl, alkyl phenyl groups and mixtures thereof in which said alkyl groups contain from 8 to 18 carbon atoms; said alkyl group being either saturated or unsaturated and containing from 0 to 3 hydroxy groups, R' is ethylene, propylene and/or glyceryl, t is from 0 to 30, and x is a number from 1.5 to 10;

(2) an anionic cosurfactant selected from the group consisting of sulfates, sulfonates, carboxylates and mixtures thereof, neutralized with one or more cationic moieties, the weight ratio of (2) to (1) being from 1:10 to 10:1 except that:

(1) the weight ratio of (2) to (1) is superior to 1:1 when the anionic surfactant is an alkali metal alkylbenzenesulfonate and when in the general formula for the alkylpolysaccharide $t=0$ and Z is a glycoside radical,

(2) the weight ratio of (2) to (1) is at least 1:2 when the anionic cosurfactant is soap; and

(3) when the anionic cosurfactant does not contain a sulfonate or carboxylate it must be from 1.5 to 3 and the alkylpolysaccharide surfactant must have a free fatty alcohol content of less than 2% by weight.

2. The composition of Claim 1 wherein the cosurfactant is selected from the group consisting of alkylbenzene sulfonates, alpha-olefin sulfonates, alkyl sulfates and paraffin sulfonates and wherein the cationic moiety is selected from the group consisting of sodium, potassium, ammonium, monoethanolammonium, diethanolammonium, triethanolammonium, calcium, magnesium and mixtures thereof.

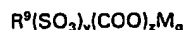
3. The composition of Claim 2 wherein the cosurfactant is an alkylbenzene sulfonate.

4. The composition of Claim 3 wherein the phenyl portion of the alkylbenzene sulfonate is attached near the middle of the alkyl chain and the cationic moiety is magnesium.

5. The composition of Claim 2 wherein the cosurfactant is an alpha-olefin sulfonate.

6. The composition of Claim 2 wherein the cosurfactant is a paraffin sulfonate.

7. The composition of Claim 1 wherein the anionic cosurfactant has the formula



wherein R^q is an alkyl, alkylphenyl, hydroxyalkylphenyl or hydroxylalkyl or mixtures thereof, said alkyl groups containing from 6 to 30 carbon atoms; wherein y is a number from 0 to 4, z is a number from 0 to 4, $y+z$ is at least 1 and wherein M is a cationic moiety with q being selected to complete the formula, x is from 1.5 to 3 and the alkyl polysaccharide surfactant has a free fatty alcohol content of less than 2% by weight.

8. The composition of Claim 7 wherein y is 0; z is 1; and wherein the cationic moiety is selected from the group consisting of sodium, potassium, ammonium, monoethanolammonium, diethanolammonium, triethanolammonium, calcium, magnesium and mixtures thereof.

9. The composition of Claims 1-6, wherein x is a number from 1.5 to 4.

10. The composition of Claim 7 wherein R^q contains a quaternary ammonium group, $y+z$ is equal to 1, and q is equal to 0.

11. A light-duty liquid detergent composition comprising from 5% to 50% by weight of the surfactant mixture of Claim 1 and from 1% to 50% by weight of a solvent selected from the group consisting of C_{1-3} alkanols, C_{1-3} alkanolamines, C_{2-4} polyols, and mixtures thereof, and the balance water.

12. The composition of Claim 11 wherein the cosurfactant is selected from the group consisting of alkylbenzene sulfonates, alpha-olefin sulfonates, alkyl sulfates and paraffin sulfonates and the cationic moiety is selected from the group consisting of sodium, potassium, ammonium, monoethanolammonium, diethanolammonium, triethanolammonium, calcium, magnesium and mixtures thereof.

13. The composition of Claim 12 wherein the cosurfactant is an alkylbenzene sulfonate.

14. The composition of Claim 13 wherein the cationic moiety is magnesium.

15. The composition of Claim 12 wherein the cosurfactant is an alpha-olefin sulfonate.

16. The composition of Claim 12 wherein the cosurfactant is a paraffin sulfonate.

17. The composition of Claim 12 wherein x is a number from 1.5 to 4.

18. The composition of Claim 12 wherein x is a number from 1.6 to 2.7.

19. A shampoo composition comprising from 1% to 95% of the surfactant mixture of Claim 1.

20. The composition of Claim 19 wherein the cosurfactant is selected from the group consisting of alkylbenzene sulfonates, alpha-olefin sulfonates, alkyl sulfates and paraffin sulfonates and wherein M is selected from the group consisting of sodium, potassium, ammonium, monoethanolammonium, diethanolammonium, triethanolammonium, calcium, magnesium and mixtures thereof.

21. The process of drilling an oil well in which water and soil particles are carried from the bore hole utilizing a foam containing from about 0.01% to about 5% of the surfactant composition of Claim 1.

22. The process of protecting plants from freezing by covering them with a foam containing the surfactant composition of Claim 1.

23. The process of concentrating ore by foaming an aqueous suspension of said ore using the surfactant composition of Claim 1.

24. The process of fighting fires utilizing a foam prepared from an aqueous solution containing from about 0.1% to about 5% of the surfactant composition of Claim 1.

25. The process of forming solid foam structures using an aqueous composition containing the surfactant composition of Claim 1.

Patentansprüche

1. Eine schäumende Zusammensetzung, enthaltend
(1) ein Alkylpolysaccharid-grenzflächenaktives Mittel mit der Formel:



5 worin Z ein von einem reduzierenden, 5 bis 6 Kohlenstoffatome enthaltenden Saccharid abgeleiteter Rest ist; R eine hydrophobe Gruppe ist, die aus der aus Alkyl-, Alkylphenylgruppen, und Gemischen davon,
10 bestehenden Gruppe ausgewählt ist, wobei die genannten Alkylgruppen 8 bis 18 Kohlenstoffatome enthalten; die genannten Alkylgruppen entweder gesättigt oder ungesättigt sind und 0 bis 3 Hydroxygruppen enthalten, R' Ethylen, Propylen und/oder Glyceryl ist, t 0 bis 30 ist; und x eine Zahl von 1,5 bis 10 ist;

(2) ein anionisches co-grenzflächenaktives Mittel, ausgewählt aus der Gruppe, die aus durch einen
15 oder mehrere kationische Reste neutralisierten Sulfaten, Sulfonaten, Carboxylaten, und Gemischen davon, besteht, wobei das Gewichtsverhältnis von (2) zu (1) 1:10 bis 10:1 beträgt, mit der Maßgabe, daß:

(1) das Gewichtsverhältnis von (2) zu (1) höher als 1:1 ist, wenn das anionische co-grenzflächenaktive Mittel ein Alkalimetallalkylbenzolsulfonat ist, und wenn in der allgemeinen Formel für das Alkylpolysaccharid $t=0$ und Z ein Glykosidrest ist;

20 (2) das Gewichtsverhältnis von (2) zu (1) wenigstens 1:2 beträgt, wenn das anionische co-grenzflächenaktive Mittel Seife ist; und

(3) wenn das anionische co-grenzflächenaktive Mittel kein Sulfonat oder Carboxylat enthält, 1,5 bis 3 betragen muß, und das Alkylpolysaccharid-grenzflächenaktive Mittel einen Gehalt an freiem Fettalkohol von weniger als 2 Gew.-% aufweisen muß.

25 2. Die Zusammensetzung des Anspruchs 1, wobei das co-grenzflächenaktive Mittel aus der Gruppe ausgewählt ist, die aus Alkylbenzolsulfonaten, α -Olefin sulfonaten, Alkylsulfaten und Paraffinsulfonaten besteht, und wobei der kationische Rest aus der Gruppe ausgewählt ist, die aus Natrium, Kalium, Ammonium, Monoethanolammonium, Diethanolammonium, Triethanolammonium, Calcium, Magnesium, und Gemischen davon, besteht.

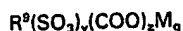
30 3. Die Zusammensetzung des Anspruchs 2, wobei das co-grenzflächenaktive Mittel ein Alkylbenzolsulfonat ist.

4. Die Zusammensetzung des Anspruchs 3, wobei der Phenylteil des Alkylbenzolsulfonats nahe der Mitte der Alkylkette gebunden ist, und der kationische Rest Magnesium ist.

35 5. Die Zusammensetzung des Anspruchs 2, wobei das co-grenzflächenaktive Mittel ein α -Olefin sulfonat ist.

6. Die Zusammensetzung des Anspruchs 2, wobei das co-grenzflächenaktive Mittel ein Paraffinsulfonat ist.

7. Die Zusammensetzung des Anspruchs 1, wobei das anionische co-grenzflächenaktive Mittel die Formel



45 hat, worin R^y ein Alkyl, Alkylphenyl, Hydroxyalkylphenyl oder Hydroxyalkyl, oder Gemische davon, ist, wobei die genannten Alkylgruppen 6 bis 30 Kohlenstoffatome enthalten; worin y eine Zahl von 0 bis 4 ist, z eine Zahl von 0 bis 4 ist, $y+z$ wenigstens 1 ist, und worin M ein Kationischer Rest mit einem zur Vervollständigung der Formel ausgewählten Wert von q ist, x 1,5 bis 3 ist, und das Alkylpolysaccharid-grenzflächenaktive Mittel einen Gehalt an freiem Fettalkohol von weniger als 2 Gew.-% aufweist.

50 8. Die Zusammensetzung des Anspruchs 7, worin y 0 ist; z 1 ist; und worin der kationische Rest aus der Gruppe ausgewählt ist, die aus Natrium, Kalium, Ammonium, Monoethanolammonium, Diethanolammonium, Triethanolammonium, Calcium, Magnesium, und Gemischen davon, besteht.

9. Die Zusammensetzung der Ansprüche 1 bis 6, worin x eine Zahl von 1,5 bis 4 ist.

10. Die Zusammensetzung des Anspruchs 7, worin R^y eine quaternäre Ammoniumgruppe enthält, $y+z$ gleich 1 ist, und q gleich 0 ist.

55 11. Eine flüssige Feinwaschmitteldetergenezusammensetzung, enthaltend 5 Gew.-% bis 50 Gew.-% des Gemisches grenzflächenaktiver Mittel von Anspruch 1 und 1 Gew.-% bis 50 Gew.-% eines Lösungsmittels, ausgewählt aus der aus C_{1-3} -Alkanolen, C_{1-3} -Alkanolaminen, C_{2-4} -Polyolen, und Gemischen davon, bestehenden Gruppe, während der Rest Wasser ist.

60 12. Die Zusammensetzung des Anspruchs 11, wobei das co-grenzflächenaktive Mittel aus der Gruppe ausgewählt ist, die aus Alkylbenzolsulfonaten, α -Olefin sulfonaten, Alkylsulfaten und Paraffinsulfonaten besteht, und der kationische Rest aus der Gruppe ausgewählt ist, die aus Natrium, Kalium, Ammonium, Monoethanolammonium, Diethanolammonium, Triethanolammonium, Calcium, Magnesium, und Gemischen davon, besteht.

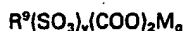
13. Die Zusammensetzung des Anspruchs 12, wobei das co-grenzflächenaktive Mittel ein Alkylbenzolsulfonat ist.

65 14. Die Zusammensetzung des Anspruchs 13, wobei der kationische Rest Magnesium ist.

15. Die Zusammensetzung des Anspruchs 12, wobei das co-grenzflächenaktive Mittel ein α -Olefin sulfonat ist.
16. Die Zusammensetzung des Anspruchs 12, wobei das co-grenzflächenaktive Mittel ein Paraffinsulfonat ist.
- 5 17. Die Zusammensetzung des Anspruchs 12, wobei x eine Zahl von 1,5 bis 4 ist.
18. Die Zusammensetzung des Anspruchs 12, wobei x eine Zahl von 1,6 bis 2,7 ist.
19. Eine Shampooszusammensetzung, enthaltend 1% bis 95% des Gemisches grenzflächenaktiver Mittel von Anspruch 1.
20. Die Zusammensetzung des Anspruchs 19, wobei das co-grenzflächenaktive Mittel aus der Gruppe ausgewählt ist, die aus Alkylbenzolsulfonaten, α -Olefin sulfonaten, Alkylsulfaten und Paraffinsulfonaten besteht, und wobei M aus der Gruppe ausgewählt ist, die aus Natrium, Kalium, Ammonium, Monoethanolammonium, Diethanolammonium, Triethanolammonium, Calcium, Magnesium, und Gemischen davon, besteht.
- 10 21. Das Verfahren zum Erbohren eines Ölbohrloches, bei dem Wasser und Erdbodenteilchen unter Verwendung eines etwa 0,01% bis etwa 5% der grenzflächenaktive Verbindungen enthaltenden Zusammensetzung von Anspruch 1 enthaltenden Schaumes aus dem Bohrloch gefördert werden.
- 15 22. Das Verfahren zum Schutz von Pflanzen gegen Erfrieren, bei dem diese mit einem Schaum bedeckt werden, welcher die grenzflächenaktive Verbindungen enthaltende Zusammensetzung von Anspruch 1 enthält.
- 20 23. Das Verfahren zur Anreicherung von Erz durch Verschäumen einer wässrigen Suspension des genannten Erzes unter Verwendung der grenzflächenaktive Verbindungen enthaltenden Zusammensetzung von Anspruch 1.
24. Das Verfahren zur Feuerbekämpfung unter Verwendung eines Schaumes, der aus einer etwa 0,1% bis etwa 5% der grenzflächenaktive Verbindungen enthaltenden Zusammensetzung von Anspruch 1 enthaltenden, wässrigen Lösung hergestellt ist.
- 25 25. Das Verfahren zur Bildung fester Schaumstrukturen unter Verwendung einer wässrigen Zusammensetzung, welche die grenzflächenaktive Verbindungen enthaltende Zusammensetzung des Anspruchs 1 enthält.

30 Revendications

1. Composition moussante comprenant
- 35 (1) un tensioactif alkylpolysaccharide ayant la formule $RO(R^1O)_xZ$, dans laquelle Z est un fragment dérivant d'un saccharide réducteur contenant de 5 à 6 atomes de carbone; R est un groupe hydrophobe choisi dans le groupe comprenant les groupes alkyle, alkylphényle et leurs mélanges, où lesdits groupes alkyle contiennent de 8 à 18 atomes de carbone; lesdits groupes alkyle étant saturés ou insaturés et contenant de 0 à 3 groupes hydroxy, R^1 est l'éthylène, le propylène et/ou le radical glycéryle, t vaut de 0 à 30; et x est un nombre de 1,5 à 10;
- 40 (2) un cotensioactif anionique choisi dans le groupe comprenant les sulfates, sulfonates, carboxylates et leurs mélanges, neutralisés par un ou plusieurs fragments cationiques, le rapport pondéral de (2) à (1) étant de 1:10 à 10:1, sauf que
- (1) le rapport pondéral de (2) à (1) est supérieur à 1:1 quand le cotensioactif anionique est un alkylbenzènesulfonate d'un métal alcalin, et quand, dans la formule générale de l'alkylpolysaccharide, t=0
- 45 et Z est un radical glycoside;
- (2) le rapport pondéral de (2) à (1) est d'au moins 1:1 quand le cotensioactif anionique est un savon; et
- (3) quand le cotensioactif anionique ne contient ni sulfonate, ni carboxylate, x doit valoir de 1,5 à 3, et le tensioactif alkylpolysaccharide doit avoir une teneur en alcool gras libre inférieure à 2% en poids.
- 50 2. Composition selon la revendication 1, dans laquelle le cotensioactif est choisi dans le groupe comprenant les alkylbenzènesulfonates, les α -oléfin sulfonates, les alkylsulfates et les paraffinesulfonates, et dans laquelle le fragment cationique est choisi dans le groupe comprenant le sodium, le potassium, l'ammonium, le monoéthanolammonium, le diéthanolammonium, le triéthanolammonium, le calcium, le magnésium et leurs mélanges.
3. Composition selon la revendication 2, dans laquelle le cotensioactif est un alkylbenzènesulfonate.
- 55 4. Composition selon la revendication 3, dans laquelle le fragment phényle de l'alkylbenzènesulfonate est fixé au voisinage du milieu de la chaîne alkyle, le fragment cationique étant le magnésium.
5. Composition selon la revendication 2, dans laquelle le cotensioactif est un α -oléfin sulfonate.
6. Composition selon la revendication 2, dans laquelle le cotensioactif est un paraffinesulfonate.
7. Composition selon la revendication 1, dans laquelle le cotensioactif anionique a la formule



dans laquelle R^q est un radical alkyle, alkylphényle, hydroxyalkylphényle ou hydroxyalkyle ou leurs mélanges, lesdits groupes alkyle contenant de 6 à 30 atomes de carbone; dans laquelle y est un nombre de

65 0 à 4, z est un nombre de 0 à 4, y+z vaut au moins 1, et dans laquelle M est un fragment cationique, q étant

choisi de façon à compléter la formule, x vaut de 1,5 à 3 et le tensioactif alkylpolysaccharide présente une teneur en alcool gras libre inférieure à 2% en poids.

8. Composition selon la revendication 7, dans laquelle y vaut 0; z vaut 1; et dans laquelle le fragment cationique est choisi dans le groupe comprenant le sodium, le potassium, l'ammonium, le monoéthanolammonium, le diéthanolammonium, le triéthanolammonium, le calcium, le magnésium et leurs mélanges.

9. Composition selon les revendications 1-6, dans laquelle x est un nombre de 1,5 à 4.

10. Composition selon la revendication 7, dans laquelle R³ contient un groupe ammonium quaternaire y+z vaut 1, et q vaut 0.

11. Composition détergente liquide pour lavage délicat, comprenant de 5 à 50% en poids du mélange de tensioactifs de la revendication 1 et de 1 à 50% en poids d'un solvant choisi dans le groupe comprenant les alcanols en C₁₋₃, les alcanolamines en C₁₋₃, les polyols en C₂₋₄ et leurs mélanges, les reste étant de l'eau.

12. Composition selon la revendication 11, dans laquelle le cotensioactif est choisi dans le groupe comprenant les alkylbenzènesulfonates, les alpha-oléfine-sulfonates, les alkylsulfates et les paraffinesulfonates, le fragment cationique étant choisi dans le groupe comprenant le sodium, le potassium, l'ammonium, le monoéthanolammonium, le diéthanolammonium, le triéthanolammonium, le calcium, le magnésium et leurs mélanges.

13. Composition selon la revendication 12, dans laquelle le cotensioactif est un alkylbenzènesulfonate.

14. Composition selon la revendication 13, dans laquelle le fragment cationique est le magnésium.

15. Composition selon la revendication 12, dans laquelle le cotensioactif est un alpha-oléfinesulfonate.

16. Composition selon la revendication 12, dans laquelle le cotensioactif est un paraffinesulfonate.

17. Composition selon la revendication 12, dans laquelle x est un nombre de 1,5 à 4.

18. Composition selon la revendication 12, dans laquelle x est un nombre de 1,6 à 2,7.

19. Composition de shampoing comprenant de 1 à 95% du mélange de tensioactifs, de la revendication 1.

20. Composition selon la revendication 19, dans laquelle le cotensioactif est choisi dans le groupe comprenant les alkylbenzènesulfonates, les alpha-oléfinesulfonates, les alkylsulfates et les paraffinesulfonates, et dans laquelle M est choisi dans le groupe comprenant le sodium, le potassium, l'ammonium, le monoéthanolammonium, le diéthanolammonium, le triéthanolammonium, le calcium, le magnésium et leurs mélanges.

21. Procédé de forage d'un puits de pétrole, dans lequel l'eau et les particules de sol sont évacuées du trou de sonde grâce à l'utilisation d'une mousse contenant d'environ 0,01 à environ 5% de la composition de tensioactifs de la revendication 1.

22. Procédé pour protéger les plantes contre le gel, consistant à les recouvrir d'une mousse contenant la composition de tensioactifs de la revendication 1.

23. Procédé de concentration de minéral, par moussage d'une suspension aqueuse dudit minéral, en faisant appel à la composition de tensioactifs de la revendication 1.

24. Procédé pour lutter contre les incendies, consistant à utiliser une mousse préparée à partir d'une solution aqueuse contenant d'environ 0,1 à environ 5% de la composition de tensioactifs de la revendication 1.

25. Procédé de façonnage de structures solides en mousse, consistant à utiliser une composition aqueuse contenant la composition de tensioactifs de la revendication 1.